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CANADIAN PATENT

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PRODUCTION OF HYDROGEN WITH ENRICHMENT OF
DEUTERIUM

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The invention relates to processes for producing deuterium-enriched water or deuterium-enriched hydrogen in the course of producing hydrogen from a starting material or a mixture of starting materials and water and relates to apparatus for carrying out such processes.

The object of the invention is the combination of an industrial hydrogen-producing plant, in which hydrogen is obtained for a subsequent process producing ammonia, methanol or other products, with a process for producing deuterium-enriched 10 water or hydrogen. A hydrogen-producing plant of this type is then much more economical, since deuterium is obtained from the hydrogen and can be used to produce heavy water.

The simplest process would be to bring the water of natural deuterium concentration used in hydrogen production into contact with the hydrogen liberated in the hydrogen-producing plant in order to enrich the water with deuterium. Such a process is not practical, however, since for direct 20 isotope exchange between the water supplied to the hydrogen-producing plant and the hydrogen produced in this plant there are no known catalysts which permit the temperature-dependent separating factors required for an economical yield, that is to say, the extraction of sufficient deuterium from the hydrogen supplied to the subsequent process, and sufficient enrichment of the water.

According to the present invention, a process is provided for producing deuterium enriched water or deuterium enriched hydrogen, characterized in that hydrogen is produced by a chemical reaction between water and a starting material or a mixture of starting materials, further characterized in that 30 water of natural deuterium concentration is brought into chemical isotope exchange in close contact with an enriched exchange medium, the water thus enriched being vaporized and being chemically

reacted in vapour form with the starting material or the mixture of starting material, said process being further characterized in that the hydrogen produced in course of the chemical reaction is brought into chemical isotope exchange in cross flow with the exchange medium depleted by the foregoing isotope exchange with water whereby the hydrogen is depleted and the exchange medium is enriched, the exchange medium being a substance different from water and containing a catalyst in dissolved form for the isotope exchange with hydrogen.

10 Advantageously, the invention can be applied to hydrogen-producing plants in which hydrogen is obtained from carbon-containing starting materials or mixtures of materials, for example natural gas, the hydrogen being produced for ammonia synthesis, for example.

Suitable exchange media are, for example, hydrogen sulphide, alcohols and ammonia; in cases in which more than one exchange medium is used, and may be selected from this list and hydrogen may advantageously be used as the medium brought into direct isotope exchange with water, although, as will be explained below, this hydrogen is not identical with the hydrogen liberated in the hydrogen-producing plant. Advantageously, particularly to give a relatively high reaction speed, at least one constituent of a medium used as exchange medium satisfies the formula



R signifying hydrogen or an alkyl group with at most five carbon atoms and R' an alkyl group with at most five carbon atoms.

Suitable exchange media which satisfy this formula are methyl amine, ethyl amine, propyl amine, butyl amine and amyl amine in all the various isomeric forms and the corresponding secondary aliphatic amines such as dimethyl amine, diethyl amine and the higher homologues which have up to five carbon atoms in each alkyl group.

Advantageously, a compound used as catalyst for isotope exchange satisfies the formula $\text{MeN}^{\text{R}}_{\text{R}^{\prime}}$. Suitable catalysts are, for example, potassium methyl amide, potassium dimethyl amide, sodium methyl amide, sodium dimethyl amide, lithium methyl amide, lithium dimethyl amide, potassium ethyl amide, potassium diethyl amide, sodium ethyl amide, sodium diethyl amide, lithium ethyl amide, or lithium diethyl amide. The catalyst may, for example, be used in the form of a concentrated solution in the intermediate carrier.

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If appropriate one of the exchange media mentioned above may merely be one constituent of a mixture with a medium of some other kind.

In one particular form of the process of the invention, only one exchange medium is used and this carrier is deuterium-depleted by isotope exchange with water and is then run in counter-current with the hydrogen liberated during hydrogen production and is deuterium-enriched by isotope exchange with this hydrogen, before being again brought into isotope exchange with the first intermediate carrier.

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The present invention also includes an apparatus suitable for carrying out a process as claimed in claim 1 comprising a hydrogen producing plant, at least one exchanger for the deuterium-enrichment of water by isotope exchange with an exchange medium and at least one exchanger for the deuterium-enrichment of an exchange medium by isotope exchange with the hydrogen from the hydrogen producing plant.

Because, in the process of the invention, the transfer of deuterium from the liberated hydrogen to water does not involve direct isotope exchange between these

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two media, but takes place with the help of at least one exchange medium, it is possible, using known catalysts and favourable, freely chosen isotope exchange temperatures, to produce an extremely high deuterium yield and a high degree of deuterium enrichment of the water, and therefore to provide a highly economical industrial apparatus.

The invention may be carried into practice in various ways and two hydrogen-producing plants and their mode of operation will now be described by way of example with reference 10 to the accompanying drawings, in which:

Figure 1 shows a plant in which only one exchange medium is used; and

Figure 2 shows a modified form of plant using two exchanged media.

The drawings are purely diagrammatic and, for the sake of clarity, those elements of the plant which are not essential to a comprehension of the invention, for example heat exchangers, pumps, compressors and the like, are omitted.

In the plant shown in Figure 1 hydrogen-producing 20 apparatus 1 is supplied by a line 1a with a hydrocarbon or a hydrocarbon mixture, which is made to react with steam supplied along a line 2. The plant is of conventional construction and consists essentially of a "reformer" and a converter. The hydrogen liberated is removed from the plant along a line 3 with further separation products and possibly steam. The separation products and the steam can then be separated by known means (not shown), preferably situated on the flow route of the liberated hydrogen.

Water of natural deuterium concentration is fed along

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a line 4 into an exchanger 5 and there brought into isotope exchange with a gaseous or vaporous exchange medium, in this example ammonia vapour, run in countercurrent. Fractionating columns 6, 7 are provided in the flow paths of the ammonia and water at the two opposite ends of the exchanger and serve to separate the ammonia and water. The separating plants are necessary when the intermediate carrier is water-soluble.

The apparatus has another exchanger 8 in which the liberated hydrogen and liquified ammonia running in counter-current with it undergo isotope exchange. Whereas no catalyst is required for isotope exchange between water and ammonia in exchanger 5, potassium amide may be used as a catalyst in exchanger 8.

A further exchanger 9 is provided for transferring deuterium from the ammonia which remains in liquid form in an evaporator 10, and which contains the catalyst, to ammonia vapour from the fractionating column 7. Before the ammonia reaches the exchanger 9, a part of the flow is diverted, condensed in a condenser 11 and combined with the deuterium-depleted ammonia and catalyst mixture leaving exchanger 9. An evaporator 12 is provided upstream of the plant 1 in the line 2. In the plant possible connections for units for extracting deuterium-enriched feed in order to produce heavy water are shown diagrammatically. These units are designated 13, 14 and 15, the feed extraction lines 13a, 14a and 15a and the return lines for depleted feed 13b, 14b and 15b. The heavy-water producing unit or units may be of conventional design, and the invention is not restricted to a particular form of such units. As far as the invention is concerned,

for example, it does not matter whether one or more further enrichment stages are provided in the apparatus upstream of a unit in which the heavy water is finally obtained.

The process carried out in Figure 1 operates as follows.

Water from a natural source, for example a lake, is supplied under pressure to the exchanger 5, through which it passes in counter-current with the ammonia fed in vapour form to the exchanger along a line 16. When this ammonia enters the exchanger, it may be deuterium-enriched to, for example, approximately sixty times the natural deuterium concentration. The natural deuterium concentration, of course, is designated N. The operating temperature of the exchanger may, for example, be about 30°C and the operating pressure about 20 atm. Since ammonia is water-soluble the ammonia is separated from the water in the fractionating column 6 and fed back to the exchanger as vapour. The water which leaves the fractionating column, and which is enriched, for example, to about 30 N, is evaporated in the evaporator 12 and brought into contact with a hydrocarbon, for example methane, in the hydrogen-producing plant 1. In this plant the hydrocarbon and steam are separated into their constituents in a known manner. Since economic considerations make it desirable to minimise the quantity of carbon monoxide obtained when cracking hydrocarbons by means of steam, the reformer is followed by a converter in which the carbon monoxide produced in the reformer is oxidized. Since the hydrogen contained in the hydrocarbons has a natural deuterium concentration, in con-

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trast to the steam which is enriched, for example, to 60 N, the concentration in the liberated hydrogen is lower than that in the steam. In the numerical example it is assumed that the concentration in the liberated hydrogen is 15 N, the water having previously been enriched to 60 N. The hydrogen now flows to the exchanger 8, whose operating temperature is for example -30°C. and whose operating pressure is approximately 100 atm. In this exchanger deuterium is transferred from the hydrogen to ammonia vapour running in countercurrent with it. In relation to the 10 numerical example, the hydrogen may be depleted to, for example, 0.21 N and then removed for use elsewhere, e.g. in an ammonia synthesis plant.

The ammonia flowing through the exchanger 8 follows a closed circuit through this exchanger and the exchanger 5. The ammonia vapour depleted to, for example, about 1.05 N in exchanger 5 is first fed to the fractionating column 7. Here the ammonia and water are separated. While the water produced as bottom product is recycled into the exchanger 5, some of the ammonia is fed to the exchanger 9. In this exchanger deuterium 20 is transferred to the ammonia vapour by isotope exchange with some of the ammonia which has been enriched from, for example, about 1.05 N to 60 N in the exchanger 8 and which has remained liquid in the evaporator 10, with the help of the catalyst, e.g. potassium amide, dissolved in this ammonia. The liquid ammonia and catalyst are depleted to 1.05 N and are then combined with the ammonia which was not fed to the exchanger 9, and which has been condensed in a condenser 11, whereupon they are returned to the exchanger 8. The ammonia vapour which leaves the exchanger

9, and which has been enriched to at least about 60 N, again undergoes isotope exchange with water in the exchanger 5, together with the ammonia with a deuterium concentration of for example 60 N evaporated in the evaporator 10.

As already explained, the extraction lines 13a, 14a, 15a, and return lines 13b, 14b, 15b represent places in the apparatus to which heavy-water producing units may be connected. The choice of these connections depends on the particular case, and the invention is by no means restricted to particular

10 locations.

As is clear from the numerical example, a separation factor of approximately 5 is obtained between the water of natural deuterium concentration and the hydrogen supplied for further use, which leaves the exchanger 8 with a deuterium concentration of 0.21 N. The required separation factor between the water of natural deuterium concentration and the liberated hydrogen is obtained without, however, bringing the water and hydrogen into direct contact for the purpose of isotope exchange. The temperature at which isotope exchange takes place between

20 the water and the intermediate carrier determines the water/hydrogen separation factor governing the yield for the apparatus as a whole.

The numerical example also shows how the invention permits a high deuterium yield, which is equivalent to high efficiency. The components of the heavy-water-producing unit can be made smaller due to the relatively high deuterium concentration obtainable for the feed, and the power consumption can be reduced to a level much below that of apparatus receiving feed of natural deuterium concentration.

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Even apparatus of the latter type, however, is made much more profitable since heavy water can be obtained almost as a by-product from industrial plant producing hydrogen for a subsequent process, for example ammonia synthesis.

If desired, the deuterium enrichment of the feed may be further increased by means of a "cascade" arrangement. For example, a further enrichment stage, identical in construction to the apparatus shown in Figure 1, can be connected to the flow path of the water from the exchanger 5, as regards the water, and to the flow path of the hydrogen liberated in the hydrogen producing plant 1, as regards the hydrogen. A plurality of such stages may, of course, be combined to form a cascade.

10 Apparatus employing two exchange media is illustrated in Figure 2.

The essential components of this apparatus are an exchanger 20 for isotope exchange between water of natural deuterium concentration and a first exchange medium, for example hydrogen, a "bithermal" stage with a hot exchanger 21 and a cold exchanger 22, and a hydrogen-producing plant 23. In this figure, also, components such as pumps, compressors, heat exchangers and the like are omitted for clarity's sake. A suitable second exchange medium is, for example, liquid ammonia.

20 The process carried out in the apparatus shown operates as follows.

Water with an initial concentration of 1 N is fed along a line 24 into the exchanger 20, whose operating temperature is, for example, 170°C, and undergoes isotope exchange with hydrogen supplied to the exchanger with a concentration of approximately 20 N. The water is enriched to about 30 N and then evaporated in an evaporator 25 before flowing to the plant 23, in which, due to a reaction with carbon-containing starting material fed in along a line 23a, hydrogen is produced whose deuterium

concentration may, for example be 12 N. In the cold exchanger 22, operated at a temperature of, for example, -30°C, this hydrogen yields deuterium to the liquid ammonia forming the second exchange medium and is depleted to approximately 0.3 N. The ammonia, enriched to about 60 N, flows to the hot exchanger where it is depleted to 1.5 N by isotope exchange with the hydrogen leaving the exchanger 20. The ammonia then returns to the exchanger 22 to receive more deuterium from the hydrogen produced. Whereas the ammonia traverses both the exchangers in the bi-
10 thermal stage and flows in a closed circuit, the circuit for the first exchange medium (hydrogen in this example contains the exchangers 20 and 21). The water content of the hydrogen depleted to 0.5 N in the exchanger 20 is separated in a liquid separator 26 and introduced into the line 24. The hydrogen now undergoes isotope exchange with ammonia in the hot exchanger, which is operated at a temperature of, for example, 55°C, and is enriched to about 20 N before returning to the exchanger 20 to transfer deuterium to water. Beforehand liquid ammonia is separated from it in a liquid separator 27 and combined with the ammonia supplied to the exchanger 21.

20 Sodium hydroxide may be used as catalyst in exchanger 20 and potassium amide in exchangers 21 and 22.

Enriched feed for the production of heavy water may, for example, as in Figure 1, be extracted from the enriched water before the latter enters the plant 23 or alternatively from the ammonia circuit after it leaves the exchanger 22 and before it enters the exchanger 21.

30 An advantage of the apparatus shown in Figure 2 is that hydrogen can be used as exchange medium in the exchanger 20, and since hydrogen is not water-soluble no fractionating columns are needed to separate the two media undergoing isotope exchange. As the numerical example shows, this apparatus, also,

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can give a required separation factor, a high degree of enrichment of the feed and a high yield, that is high deuterium completion of the hydrogen supplied for a subsequent process.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for producing deuterium enriched water or deuterium enriched hydrogen, characterized in that hydrogen is produced by a chemical reaction between water and a starting material or a mixture of starting materials, further characterized in that water of natural deuterium concentration is brought into chemical isotope exchange in cross flow with an enriched exchange medium, the water thus enriched being vaporized and being chemically reacted in vapour form with the starting material or the mixture of starting material, said process being further characterized in that the hydrogen produced in course of the chemical reaction is brought into chemical isotope exchange in cross flow with the exchange medium depleted by the foregoing isotope exchange with water whereby the hydrogen is depleted and the exchange medium is enriched, the exchange medium being a substance different from water and containing a catalyst in dissolved form for the isotope exchange with hydrogen.

2. A process as claimed in claim 1 in which the hydrogen is obtained by means of a reaction between water and a carbon-containing starting material or mixture of materials.

3. A process as claimed in claim 1 or claim 2 in which hydrogen sulphide is used as the exchange medium.

4. A process as claimed in claim 1 or claim 2 in which an alcohol is used as the exchange medium.

5. A process as claimed in claim 1 or claim 2 in which ammonia is used as the exchange medium.

6. A process as claimed in claim 1 or claim 2 in which at least one constituent of the exchange medium satisfies the formula $\text{HN} < \text{R}'$

R' signifying hydrogen or an alkyl group with at most five carbon atoms and R' an alkyl group with at most five carbon atoms.

7. A process as claimed in claim 1 in which the isotope exchange is assisted by a catalyst comprising or containing a compound which satisfies the formula $\text{MeN}^R_{R'}$.

Me signifying an alkali metal, R signifying hydrogen or an alkyl group with at most five carbon atoms and R' an alkyl group with at most five carbon atoms.

8. A process as claimed in claim 1 in which isotope exchange between water and the exchange medium and isotope exchange between the liberated hydrogen and the exchange medium take place at different temperatures.

9. Apparatus suitable for carrying out a process as claimed in claim 1 comprising a hydrogen producing plant, at least one exchanger for the deuterium enrichment of water by isotope exchange with an exchange medium and at least one exchanger for the deuterium enrichment of an exchange medium by isotope exchange with the hydrogen from the hydrogen producing plant.

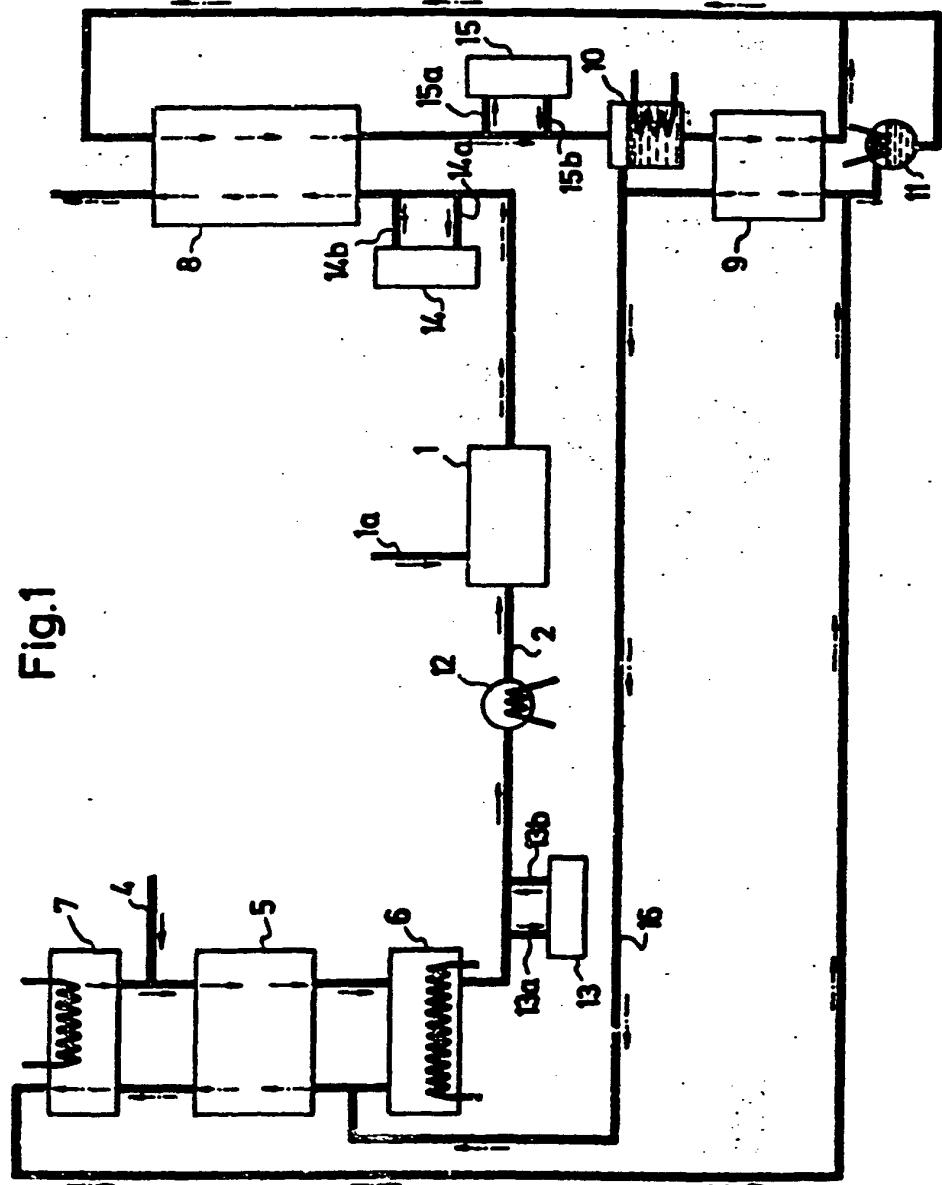
10. Apparatus as claimed in claim 9 in which a single exchange medium is used, the exchanger traversed in counter-current by water and the exchange medium being so situated on the flow route for the exchange medium that the latter runs in a closed circuit through this exchanger and the exchanger for isotope exchange with the liberated hydrogen, a condenser being provided on the flow route for the exchange medium between its outlet from the exchanger traversed by water and its inlet into the exchanger traversed by liberated hydrogen, and an evaporator being provided between the exchange medium outlet from the exchanger traversed by the liberated hydrogen and the inlet of the exchanger traversed by water.

11. Apparatus as claimed in claim 10 which is adapted for use with a water-soluble exchange medium and which includes a fractionating column associated with each end of the exchanger traversed by water and the exchange medium.

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Fig.2

